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(54) OXIDE IONIC CONDUCTOR AND USE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an oxide ionic conductor having high heat resistance, scarcely being influenced by an oxygen partial pressure and capable of manifesting high oxide ionic (mixed) conductivity by providing a composition in which a part of the site A in a rare earth gallate-based oxide represented by ABO3 of a perovskite type structure is replaced with an alkaline earth metal and a part of the site B therein is replaced with a nontransition metal such as Mg.

SOLUTION: This oxide ionic conductor is represented by the general formula: Ln1-xAxGa1-y-zB1yB2zO3 {Ln is one more kinds of La, Ce, Pr, Nd and Sm; A is one or more kinds of Sr, Ca and Ba; B1 is one or more kinds of Mg, Al and In; B2 is one or more kinds of Co, Fe, Ni and

Cu; (x) is 0.05-0.3; (y) is 0-0.29; (z) is 0.01-0.3; [(y)+(z)] is 0.025-0.3}. The oxide ionic conductor is useful as an electrolyte for a solid oxide type fuel cell, a gas sensor such as an oxygen sensor and an oxygen separation membrane for an electrochemical type oxygen pump.

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CLAIMS

[Claim(s)]

[Claim 1] A general formula: Ln1-x Ax Ga1-y-z B1y B-2 z O3 An oxide ion conductor shown. One sort or two sorts or more of the inside of a formula, Ln=La, and Ce, Pr, Nd and Sm; one sort or more than 2 sort;x=0.05-0.3 of one sort of one-sort or two or more sort;B1=Mg of A=Sr, and calcium and Ba, and aluminum and In or more than 2 sort;B-2=Co, and Fe, nickel and Cu ; y=0-0.29;z=0.01-0.3 ; y+z= 0.025-0.3.

[Claim 2] A high oxide ion conductor of oxide ion conductivity which is y>=0.025 and z<=0.15 according to claim 1.

[Claim 3] An oxide ion conductor according to claim 1 in which electronic-ion mixed conductivity which is z> 0.15 is shown.

[Claim 4] An oxide ion conductor according to claim 1 which are Ln=La and/or Nd, A=Sr, B1=Mg, B-2=Co, x= 0.10 to 0.25, y= 0 to 0.17, z= 0.02 to 0.15, and y+z=0.10-0.25.

[Claim 5] Ln=La, A=Sr, B1=Mg, B-2=Fe, x= 0.1-0.3, y= 0.025 to 0.29, z= 0.01 to 0.15, and y+z= 0.035-0.3 it is -- an oxide ion conductor according to claim 2.

[Claim 6] An oxide ion conductor according to claim 5 which are x= 0.15 to 0.25, y= 0.09 to 0.24, z= 0.01 to 0.05, and y+z=0.10-0.25.

[Claim 7] A solid acid ghost mold fuel cell equipped with an electrolyte which consists of an oxide ion conductor according to claim 2, 4, 5, or 6.

[Claim 8] A solid acid ghost mold fuel cell equipped with an air pole containing an oxide ion conductor according to claim 3.

[Claim 9] A solid acid ghost mold fuel cell equipped with an electrolyte which consists of an oxide ion conductor according to claim 2, 4, 5, or 6, and an air pole containing an oxide ion conductor according to claim 3.

[Claim 10] (1) nickel and (2) A general formula: Ce1-mCmO2 (the inside of a formula and C mean one sort of Sm, Gd, Y, and calcium, or two sorts or more, and are m=0.05-0.4) A solid acid ghost mold fuel cell given in any 1 term of claims 7-9 equipped with a fuel electrode which consists of a compound shown.

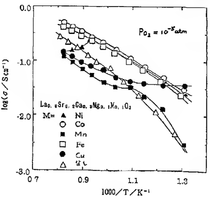
[Claim 11] A gas sensor which consists of an oxide ion conductor according to claim 2, 4, 5, or 6.

[Claim 12] A deoxygenation film for electrochemical oxygen pumping which consists of an oxide ion conductor according to claim 2, 4, 5, or 6.

[Claim 13] A gas separation membrane which consists of an oxide ion conductor according to claim 3.

[Translation done.]

Drawing selection Representative drawing



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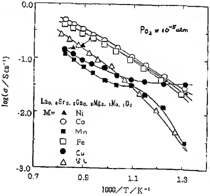
Drawing selection Representative drawing



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to the new oxide ion conductor of the rare earth gallate system which takes perovskite type structure. The oxide ion conductor of this invention shows very high oxide ion conductivity or oxide ion mixed conductivity, without seldom being influenced by oxygen tension, and is useful as deoxygenation films, such as gas sensors, such as an electrolyte of a fuel cell or an air pole, and an oxygen sensor, and electrochemistry type oxygen pumping, a gas separation membrane, etc.
[0002]
[Description of the Prior Art] Electron nature electric conduction is low and it is mainly oxide ion. (O2-) The oxide ion conductor in which electrical conductivity is shown by migration consists of a metallic oxide which doped other metals so that an O2-hole may generally be produced, and it is a solid acid ghost mold. (solid oxide type) Fuel cell (SOFC) The application to gas sensors, such as an electrolyte and an oxygen sensor, the deoxygenation film for electrochemistry type oxygen pumping, etc. has been tried.
[0003] CaO with the example of representation of an oxide ion conductor little to zirconium oxide (ZrO2), MgO, Y2O3, and Gd 2O3 etc. -- it is the solid solution of the cubic system fluorite mold called stabilized zirconia which made divalent or a trivalent metal oxide dissolve. Stabilized zirconia is the ion transference number, even if oxide ion conductivity is dominant at all the oxygen-content drafts from an oxygen ambient atmosphere to a hydrogen ambient atmosphere when excelled in thermal resistance, and oxygen tension falls. (oxide ion conductivity occupied to electrical conductivity comparatively) It is hard to fall.
[0004] Therefore, stabilized zirconia is a zirconia. (oxygen) As a sensor, they are control of various industrial processes including steel manufacture, and combustion of an automobile engine. (air-fuel ratio) It is widely used for control. Moreover, solid acid ghost mold fuel cell which operates around 1000 degrees C under development (SOFC) It is used as an electrolyte. However, highly enough, the oxide ion conductivity of stabilized zirconia runs short of conductivity, if especially temperature becomes low. for example, the ionic conductivity of Y2O3 stabilized zirconia -- 1000 degrees C -- 10-1 S/cm it is -- although -- 500 ** -- 10-4 S/cm Since it falls, service temperature is restricted to the elevated temperature more than 800 **, also by the minimum.
[0005] As a fluorite mold oxide in which the very high oxide ion conductivity which endures stabilized zirconia is shown, it is Bi 2O3. Bi 2O3 which made Y2O3 dissolve There is a system oxide. Although oxide ion conductivity is very high, since the melting out temperature is as low as 850 ** weakness, this oxide has inadequate thermal resistance. Since it will be returned even to a metal if the electron nature electric conduction of n mold will appear by change of Bi3+->Bi2+ if it is weak to a reducing atmosphere and oxygen tension moreover falls, oxygen

tension falls further and it becomes close to a pure hydrogen ambient atmosphere, it cannot be used for a solid acid ghost mold fuel cell.

[0006] Among other fluorite mold oxide ion conductors, since, as for a ThO2 system oxide, electron nature electric conduction becomes dominant with a hypoxia partial pressure the top where oxide ion conductivity is much lower than stabilized zirconia, the ion transference number falls remarkably. For a CeO2 system oxide, although the oxide ion conductivity which endures stabilized zirconia is shown, oxygen tension is 10-12. If it falls below in an atmospheric pressure, the electron nature electric conduction of n mold will appear by change of Ce4+->Ce3+, and the ion transference number will fall greatly too.

[0007] As an oxide ion conductor which takes the crystal structures other than a fluorite mold, it is PbWO4, and LaAlO3 and CaTiO3. Although known, the top where oxide ion conductivity is low, by the hypoxia part draft, semiconductance appears, electron nature electric conduction mainly becomes, and, as for each of these, the ion transference number falls.

[0008]

[Problem(s) to be Solved by the Invention] Although the high oxide ion conductor of oxide ion conductivity was known from stabilized zirconia as explained above, since thermal resistance was inadequate, or electron nature electric conduction became dominant in a hypoxia partial pressure and the ion transference number fell greatly, it was not suitable for the use of the electrolyte or oxygen sensor of a solid acid ghost mold fuel cell.

[0009] Oxide ion conductivity is high still more desirable, and this invention is all the oxygen tension from an oxygen ambient atmosphere to a hydrogen ambient atmosphere, even if oxide ion conductivity higher than stabilized zirconia is shown, thermal resistance is high and temperature falls as well as an elevated temperature. (namely, oxygen tension is also low) Decline in the ion transference number is small, and oxide ion conduction is dominant or makes it a technical problem to offer the oxide ion conductor in which mixed ion conductivity is shown.

[0010]

[Means for Solving the Problem] this invention persons are ABO3 of perovskite type structure, while advancing research in order to solve the above-mentioned technical problem. (among a formula) A is one sort or two sorts or more of lanthanoids system rare earth metals, and B is Ga. In a rare earth gallate system oxide shown, it is alkaline earth metal in some rare earth metals of A site. And/or, when non-transition metals, such as Mg, In, and aluminum, replaced some Ga atoms of B site, it found out that a material in which high oxide ion conductivity is shown was obtained. Oxide ion conductivity with a material expensive especially shown with La0.8Sr0.2Ga0.8Mg 0.2O3 was shown.

[0011] A graph [the conventional oxide ion conductor / electrical conductivity / of this compound] is shown in drawing 1 . It is the Y2O3 stabilized zirconia whose La0.8Sr0.2Ga0.8Mg 0.2O3 is the conventional typical stabilized zirconia as this graph shows. It compares with CaO stabilized zirconia and is very high conductivity. (it is the same electrical conductivity and the following) It is shown. Bi 2O3 Although a system oxide shows conductivity still higher than this, as mentioned above, since it is weak to reducing atmosphere, utilization as an oxide ion conductor is difficult a top where thermal resistance is inadequate.

[0012] When this invention persons made B site of the above-mentioned rare earth gallate system oxide contain specific little transition metals as a result of investigating about a material with still higher oxide ion conductivity, oxide ion conductivity improved further and a header and this invention were reached [that high oxide ion conductivity is shown also at low temperature, and].

[0013] It is the oxide ion conductor with which this invention is shown here by the following general formula.

Ln1-x Ax Ga1-y-z B1y B-2 z O3 ... Inside of a **** type, One sort or two sorts or more (Ln=La,

and Ce, Pr, Nd and Sm); A=Sr, One sort or more than 2 sort;x=0.05-0.3 of one sort of one-sort or two or more sort;B1=Mg of calcium and Ba, and aluminum and In or more than 2 sort;B-2=Co, and Fe, nickel and Cu ; y=0-0.29;z=0.01-0.3 ; y+z= 0.025-0.3.

[0014] In this invention, an electrical conductivity material to which substantial oxide ion conductivity is indicated to be an "oxide ion conductor" is meant. That is, not only an oxide ion conductor in a narrow sense with which oxide ion conductivity occupies most electrical conductivity but a material with which both electronic conduction nature called an electronic-ion mixed conductor (or oxide ion mixed conductor) by case and oxide ion conductivity account for a big rate is included in an oxide ion conductor by this invention as a material in which oxide ion conductivity is shown.

[0015] When it is the oxide ion conductor in a narrow sense with which oxide ion conductivity occupies most electrical conductivity, it is the ion transference number. (oxide ion conductivity occupied to electrical conductivity comparatively) It is 0.7 preferably. It is above and is 0.9 more preferably. It is above. on the other hand -- a case of an electronic-ion mixed conductor -- the ion transference number -- desirable -- 0.1-0.7 -- more -- desirable -- 0.2-0.6 it is .

[0016] According to this invention, a solid acid ghost mold fuel cell which used the above-mentioned oxide ion conductor for an electrolyte or an air pole, a gas sensor which consists of this oxide ion conductor, a deoxygenation film for electrochemical oxygen pumping, and a gas separation membrane using a gas concentration difference are also offered again.

[0017]

[Embodiment of the Invention] The oxide ion conductor of this invention shown by the above-mentioned ** formula has a perovskite mold crystal structure, and is ABO3. Ln atom and A atom of the above-mentioned general formula occupied A site of the perovskite mold crystal shown, and remaining Ga atoms, B1 atoms, and B-2 atoms occupy the B site. In addition, there may not be B1 atom.

[0018] Originally it is divalent metal in a part of A and the B car site which trivalent metal occupies. (for example, the above-mentioned A atom which occupies A site, Mg of B1 which occupies B site) Or transition metals (B-2 atom which occupies B site) By occupying, an oxygen hole is produced and oxide ion conductivity appears by this oxygen hole. Therefore, as for an oxygen atomic number, only the part of this oxygen hole will decrease.

[0019] That is, although it is displayed by ** formula that an oxygen atomic number is 3, an oxygen atomic number is three or less in fact. However, the number of oxygen holes is an addition atom. (A, B1, B-2) Since it changes not only with a class but with the class and amount of temperature, oxygen tension, and B-2 atom, it is difficult to display correctly. Therefore, the numeric value of an oxygen atomic ratio is expressed as the chemical formula showing the perovskite die materials of this specification as 3 for convenience.

[0020] In upper ** type, Ln is a lanthanoids system rare earth metal, A is alkaline earth metal, B1 is non-transition metals, and B-2 is transition metals. That is, the oxide ion conductor of this invention is lanthanoids gallate. (LnGaO3) It considers as basic structure. It is alkaline earth metal to this. (A) Non-transition metals (B1) And transition metals (B-2) Three kinds, Or alkaline earth metal (A) And transition metals (B-2) 5 yuan system which doped two kinds of atoms (Ln+A+Ga+B1+B-2) Or 4 yuan system (Ln+A+Ga+B2) It is a multiple oxide. Hereafter, this multiple oxide of 5/4 yuan may be called system multiple oxide.

[0021] 4 yuan system multiple oxide of Ln+A+Ga+B1 (the example of representation is above-mentioned La0.8Sr0.2Ga0.8Mg 0.2O3) As shown in drawing 1 , it is the outstanding oxide ion conductor in which oxide ion conductivity higher than stabilized zirconia is shown. This is called contrast system multiple oxide of 4 yuan by this invention. According to this invention, they are transition metals about some or all of B1 atom of this contrast system multiple oxide of 4 yuan. (B-2 atom) By replacing, the oxide ion conductor in which oxide ion conductivity still higher than the contrast system multiple oxide of 4 yuan is generally shown is obtained.

[0022] To drawing 2 , they are transition metals in some Mg of the contrast system multiple oxide of 4 yuan of La0.8Sr0.2Ga0.8Mg 0.2O3. (in the general formula of drawing 2 , it is displayed as M) Oxide ion conductor of this invention which was replaced and was made into the system (for Sr and B1, Mg and B-2 are [Ln / La and A] M atom) Electrical conductivity is shown.
[0023] As shown in this drawing, it is B-2 atom. (the general formula of drawing 2 M) It is indicated at every temperature that electrical conductivity very higher than the contrast system multiple oxide of 4 yuan is Co or Fe. With the contrast system multiple oxide of 4 yuan, it is a low temperature side especially. (the value of a horizontal axis 1.1 above, about below 630 **) Since the conductive fall is large, in a low temperature side, the conductive improvement by content of Co or Fe becomes large. B-2 Hara (M) A horizontal axis is about 0.9 when a child is nickel. Above (about [temperature] below 840 **) It sets and conductivity comes to exceed the conductivity of the contrast system multiple oxide of 4 yuan. A horizontal axis is about 1.1 when B-2 atom is Cu. Above (about [temperature] below 630 **) It sets, even if temperature falls in what conductivity comes to exceed the conductivity of the contrast system multiple oxide of 4 yuan, and should observe it for from this, conductivity does not fall to it, but since it is almost fixed, a horizontal axis is 1.3. Above (about [temperature] below 500 **) The then highest conductivity all over drawing comes to be shown.
[0024] Therefore, it is desirable that B-2 atom uses it as an oxide ion conductor by the low temperature side comparatively in nickel or Cu. However, contrast system multiple oxide of 4 yuan made into the comparative object in drawing 2 (La0.8Sr0.2Ga0.8Mg 0.2O3) A horizontal axis is 1.0 as shown in drawing 1 . Since conductivity very higher than the elevated-temperature side which exceeds, or stabilized zirconia is shown, if B-2 atom compares with the case in nickel or Cu, or stabilized zirconia, not only a low temperature side but an elevated-temperature side can be said that conductivity is high enough.
[0025] On the other hand, a horizontal axis is 1.1 as the transition metals of B-2 atom are Mn. In the following elevated-temperatures side, conductivity is lower than the contrast system multiple oxide of 4 yuan, and a horizontal axis is 1.1. The conductive improvement by the above low temperature side or the contrast system multiple oxide of 4 yuan, and conductivity being comparable, and replacing some Mg with transition metals is substantially obtained at no temperature. Therefore, as a B-2 atom of transition metals, the conductive improvement in comparison with the contrast system multiple oxide of 4 yuan may be one sort chosen from Co, Fe, nickel, and Cu which are obtained at a part of [at least] temperature, or two sorts or more.
[0026] atomic ratio of the dope atom in each site, i.e., A atom in A site, Sum total atomic ratio of the B1 atom +B-2 atom in (x) or B site (y+z) if it becomes out of range [the above] -- the electrical and electric equipment of the 5/4 yuan system multiple oxide of this invention -- conductive -- it is -- the ion transference number falls.
[0027] Drawing 3 is A atom. (Sr) The conductivity at the time of changing a rate is shown, and it is the atomic ratio of A atom. (x) 0.05-0.3 (the atomic ratio of =Ln atom 0.7-0.95) When it separates from a range, it turns out that conductivity falls.
[0028] Drawing 4 (a) Sum total atomic ratio of a B1 atom +B-2 atom (y+z, however y:z=11.5:8.5) The conductivity at the time of making it change is shown. Conductivity increases as this total value becomes large. However, drawing 4 (b) If the value of y+z increases so that it may be shown, decline in the ion transference number will be accepted, and it is 0.3 (= the atomic ratio of Ga 0.7). When it exceeds, the ion transference number is 0.7. It comes to be less.
[0029] Electrical conductivity becomes high, so that z value which is the atomic ratio of B-2 atom (Co) increases about B-2 atom among two kinds of dope atoms of B site, as shown in drawing 5 . This is because B-2 atoms are transition metals, electron nature electric

conduction increases, so that this atom increases in number, since it is easy to discover the electron nature electric conduction of n mold or p mold by fluctuation of a valence, and electrical conductivity becomes high. It follows on it and is the rate of oxide ion conductivity. (ion transference number) It falls.

[0030] If z value is 0.15 or less 5 yuan system multiple oxide as drawing 5 shows, the ion transference number is 0.7. The ion transference number is 0.9 as it becomes the above and especially z value is 0.10 or less. It is high and functions as the above as an oxide ion conductor in a narrow sense mentioned above. However, if B1 atom which is non-transition metals is not contained to some extent to B site in this case, it is the rate of contribution of electron nature electric conduction 0.3 It is below unmaintainable. Such a material is useful as the electrolyte of a solid acid ghost mold fuel cell, a gas sensor, a deoxygenation film for electrochemical oxygen pumping, etc. so that it may mention later.

[0031] On the other hand, when z value exceeds 0.15, the ion transference number is 0.7. It falls below and comes to function as an electronic-ion mixed conductor. As mentioned above, such a material is also included into an oxide ion conductor by this invention. what should be observed -- z value -- 0.2 (namely, y value = 0) That is, Mg (B1 atom) perfect -- Co (B-2 atom) the multiple oxide of the replaced 4 yuan system -- the ion transference number -- about 0.3 remaining -- in addition -- electronic-ion mixed conductor (namely, oxide ion mixed conductor) ****** -- it fully functions, and conductivity becomes the highest as mentioned above. Such a mixed conductor is useful to the air pole or gas separation membrane of a solid acid ghost mold fuel cell so that it may mention later.

[0032] In the above-mentioned ** type, the desirable presentation is as follows. Ln=La, Nd(s) or such mixture especially La, A=Sr, B1=Mg, B-2=Co, x= 0.10 to 0.25 especially 0.17 to 0.22, y= 0 to 0.17 especially 0.09 to 0.13, y+z=0.10-0.25, especially 0.15-0.20.

[0033] z value is high oxide ion conductivity. (the ion transference number 0.7 above, preferably 0.9 above) When making it function as an oxide ion conductor in the semantics in a narrow sense which it has, it is desirable z= 0.02 to 0.15 and that it is especially 0.07-0.10. the case where he wants to make it function as an electronic-ion mixed conductor on the other hand -- z value -- 0.15< z<=0.3 it is -- it is 0.15< z<=0.25 preferably.

[0034] if it is in 1 suitable mode of this invention -- Ln=La, A=Sr, B1=Mg, B-2=Fe, x= 0.1-0.3, y= 0.025 to 0.29, z= 0.01 to 0.15, and y+z= 0.035-0.3 it is . That is, this oxide ion conductor is shown by the following ** type.

[0035]

La1-x Sr x Ga1-y-z Mg y Fe zO3 ... The inside of a ** type, x= 0.1-0.3 ; y= 0.025-0.29;z=0.01-0.15;y+z= 0.035-0.3.

[0036] ** The oxide ion conductor shown by the formula shows high electrical conductivity, without being hardly dependent on oxygen tension. The thing and 1 - 10-21 atm which only P mold semiconductance contributes to this electrical conductivity by the hyperoxia part draft Large oxygen tension (namely, oxygen tension which attains to an oxidizing atmosphere from a reducing atmosphere) Oxide ion conductivity is dominant and the ion transference number of electrical conductivity is 0.9. It is as high as the above. Thus, the high ion transference number is shown regardless of oxygen tension, and since electrical conductivity is also high to coincidence, it is thought that the improvement in the electrical conductivity of the oxide ion conductor of this invention is mainly based on the improvement in oxide ion conductivity.

[0037] 5 yuan system multiple oxide which replaced some Mg of the contrast system multiple oxide of 4 yuan shown with La0.8Sr0.2Ga0.8Mg 0.2O3 by drawing 6 by Fe (namely, La0.8Sr0.2Ga0.8Mg0.2-zFez O3) Electrical conductivity (950 **, oxygen tension =10-5 atm) It is shown. As this drawing shows, compared with the contrast system multiple oxide of 4 yuan of z= 0, if some Mg is replaced by Fe, generally electrical conductivity will become high, especially electrical conductivity is high in z=0.01-0.05, and it turns out that a peak price is

reached in the z= 0.03 neighborhood.
[0038] Drawing 7 (a) Temperature change of the electrical conductivity of the 5 yuan system multiple oxide shown by ** formula shown by La0.8Sr0.2Ga0.8Mg0.2-zFez O3 (0. z= 0.03, 05, 0.1, 0.15), and the 4 yuan system multiple oxide of z= 0 (Arrhenius plot) Drawing 7 (b) ** type shows the oxygen tension dependency of the electrical conductivity of the 5 yuan system multiple oxide of z= 0.03, and a related compound, respectively. It is 0.9 since this 5 yuan system multiple oxide shows a large temperature and electrical conductivity high in the range of oxygen tension and electrical conductivity hardly shows an oxygen tension dependency, as shown in this drawing. It turns out that the above high ion transference number is shown.
[0039] Therefore, this 5 yuan system multiple oxide is useful as the electrolyte of a solid acid ghost mold fuel cell, a gas sensor, a deoxygenation film for electrochemical oxygen pumping, etc. Since oxide ion conductivity is higher than stabilized zirconia and change by temperature or oxygen tension is small, the product which excelled stabilized zirconia in the engine performance can be given.
[0040] In the above-mentioned ** type, the desirable presentation is as follows. x= 0.15 to 0.25 -- especially -- 0.17 to 0.22, and y= 0.09 to 0.24 -- especially -- 0.10 to 0.20, and z= 0.01 to 0.05 -- especially -- about 0.03 and y+z=0.10-0.25 -- especially -- 0.15-0.22.
[0041] The oxide ion conductor of this invention can be manufactured by fabricating suitably with a means the mixture which often mixed the powder of each oxide of a component element by the predetermined blending ratio of coal, calcinating it, and making it sinter. It is the precursor which pyrolyzes during baking and becomes an oxide as raw material powder in addition to an oxide. s (an example, a carbonate, carboxylic acid, etc.) It can be used. 1200 degrees C or more of burning temperature for sintering are 1300 degrees C or more preferably, and firing time is several hours thru/or dozens of hours. In order to shorten firing time, preliminary baking of the raw material mixture may be carried out at low temperature from sintering temperature. This preliminary baking can be carried out by heating at 500-1300 degrees C for about 1 to 10 hours. If required, after grinding the mixture which carried out preliminary baking, it is fabricated and is made to sinter finally. Shaping can adopt proper fine-particles shaping means, such as uniaxial pressing, a hydrostatic-pressure press, extrusion molding, and tape cast shaping. Firing environmentses also including preliminary baking have desirable oxidizing atmospheres or inert gas ambient atmospheres, such as air.
[0042] y value among the oxide ion conductors of this invention -- 0.025 It is above and the thing of 0.15 or less 5 yuan system has [z value] dominant oxide ion conductivity in electrical conductivity. (that is, the ion transference number 0.7 above) it is -- it becomes the oxide ion conductor of the above-mentioned narrow sense. This material is the use of various kinds of oxide ion conductors with which stabilized zirconia has been used conventionally. (an example, the electrolyte of SOFC, gas sensor) It can use. This kind of this invention of oxide ion conductor has oxide ion conductivity higher than stabilized zirconia, and is expected to give the product which excelled stabilized zirconia in the engine performance, since it can operate also at low temperature.
[0043] YSZ For the applicable field of an oxide ion conductor [like], although it reaches far and wide, one of the important uses is a solid acid ghost mold. (solid oxide type) Fuel cell (SOFC) It is an electrolyte. SOFC to which development is progressing most at present -- Y2O3 stabilized zirconia (YSZ) a thin film -- an electrolyte -- carrying out -- air pole (cathode) **** -- perovskite die materials (an example, Sr content LaMnO3) which show electron nature electric conduction Fuel electrode (anode) **** -- the cell configuration using cermets, such as metals, such as nickel, or nickel-YSZ, is taken. YSZ YSZ since the increase of the generating efficiency by the cogeneration which operates a low thing and the steam turbine generator which used the heat of exhaust gas near 1000 degree C of conductivity is attained at low temperature SOFC used as an electrolyte is designed so that operating at high temperatures

may be carried out around 1000 degrees C.
[0044] The voltage drop of SOFC by electrolytic resistance loss is large, and high power is obtained for a thin film. Therefore, electrolytic YSZ It is used with the about 30-50-micrometer thin film. However, in addition, it is still YSZ. Since oxide ion conductivity is small, in order to obtain practically sufficient engine performance, it is necessary to heat at about 1000 degrees C. Thin film YSZ of 30 micrometer thickness of thickness It is reported that the practical power density in the operating temperature of 1000 degrees C is about two 0.35 W/cm. YSZ of the thinness of several micrometers thru/or about 10 micrometers in order to make the output of a cell higher than this or to make operating temperature low Although the example of an experiment which used the thin film is reported, the gas impermeability for which an electrolyte is asked in such a thin film becomes uncertain, and it is not desirable in respect of reliability.
[0045] the oxide ion conductor in a narrow sense which consists of a 5 yuan system perovskite mold oxide of this invention -- YSZ since what has very high oxide ion conductivity can be obtained -- for example, thickness 0.5 mm (= 500 mum) ** -- YSZ of the above even when SOFC is constituted using the electrolyte of the thick film which can be manufactured with the sintering process to say An output higher than a thin film can be obtained. The maximum output density in this case is YSZ of 30-micrometer thickness, although it changes also with the classes and atomic ratios of B-2 atom. Compared with SOFC using a thin film, even the operating temperature of 1000 degrees C endures this, and they are several times at the operating temperature of 800 degrees C. (an example, 3 times, or more than it) It becomes large. Or thickness 200 [about] If it uses by the film of mum, it will set at the low temperature 600 ** thru/or 700 **, and it is YSZ of 30-micrometer thickness. Power density equivalent to a film demonstrating at 1000 degrees C can be obtained.
[0046] What is necessary is just to choose the concrete material to be used according to operating temperature, when using the oxide ion conductor of this invention for the electrolyte of SOFC. For example, since the high operating temperature around 1000 degrees C is required to perform the turbine generation of electrical energy by exhaust gas to coincidence as cogeneration, it is desirable that B-2 atom in which such oxide ion conductivity high at an elevated temperature is shown uses for an electrolyte Co and Fe, and the 5 yuan system multiple oxide that is especially Co. On the other hand, if operating temperature is a 800 ** degree, that whose B-2 atom is nickel can also be used in addition to the above, and if operating temperature is below 600 ** further, B-2 atom can use what is Cu.
[0047] operating temperature -- for example, -- The generating efficiency of SOFC does not fall so much by performing the generation of electrical energy by the steam or other exhaust gas to coincidence with 600 - 700 **, even if low, or attaining the energy deployment as a heat source to coincidence. Thus, when operating temperature becomes low, ferrous materials, such as stainless steel, can be used for the structural material of SOFC, and there is also an advantage that the cost of materials decreases remarkably compared with a material called a nickel-Cr alloy and a ceramic in case operating temperature is around 1000 degrees C. the conventional YSZ **** -- although SOFC operated at such low temperature was not able to be built, according to this invention, it becomes possible [an elevated-temperature actuation mold] from such a low-temperature actuation mold to build various SOFC(s) according to an operating environment.
[0048] Since the oxide ion conductor which consists of a 5 yuan system multiple oxide shown especially by the above-mentioned ** formula has the wide temperature requirement which shows high oxide ion conductivity, it fully functions as an electrolyte of SOFC also in which temperature of the high operating temperature around 1000 degrees C from the comparatively low operating temperature 600-700 **. Therefore, when this oxide ion conductor is chosen as an electrolyte, various SOFC(s) of a low-temperature actuation mold to an elevated-temperature actuation mold can be built only with this material.

[0049] As mentioned above, the 5 yuan system multiple oxide of this invention is YSZ. Since it becomes possible to compare, to thicken an electrolyte since oxide ion conductivity is very high, for example, to manufacture from the sintered compact of a 0.5 mm degree, a mechanical strength and a life improve sharply, and moreover, it is YSZ. SOFC with maximum output density higher than the case where it considers as an electrolyte can be manufactured.
[0050] Especially the electrode of SOFC which uses the oxide ion conductor of a 5 yuan system of this invention as an electrolyte is not restricted, but can use the electrode material used for the conventional SOFC. For example, Sm0.5-0.7Sr0.3-0.5CoO3 to a fuel electrode can consist of nickel metals for an air pole. When this cell configuration is taken, especially the output in low temperature increases and 800 ** is also 1.5 W/cm2. Since the high maximum output density which exceeds is obtained and power density also with comparatively higher still 600 ** is obtained, it is expected conventionally of less than [600 ** or it] that the solid acid ghost mold fuel cell in which the impossible low-temperature actuation is possible becomes producible. The cermet of nickel-CeO2 grade is sufficient as a fuel electrode in order to reduce an electrode overvoltage. Especially about a desirable air pole and a desirable fuel electrode, it mentions later.
[0051] YSZ At present, the biggest use is an oxygen sensor, and it is used for Air Fuel Ratio Control of an automobile in large quantities, and also it is used for control of industrial processes, such as steel manufacture. This oxygen sensor is called a solid electrolyte oxygen sensor, and measures acidity concentration by the principle of an oxygen concentration cell. That is, if the difference of an oxygen gas partial pressure is in the both ends of the material which consists of an oxide ion conductor, since oxide ion is spread and an oxygen concentration cell is constituted inside a material, it becomes possible by attaching an electrode to both ends and measuring electromotive force to measure oxygen tension. A solid electrolyte oxygen sensor is SOx and NOx in addition to oxygen gas. It can use also as a sensor of the said oxygen content gas.
[0052] YSZ from -- at low temperature, although the becoming oxygen sensor was comparatively cheap, since oxide ion conductivity fell, the sensor could be used only at the elevated temperature more than 600 **, but the use was restricted. On the other hand, oxide ion conductor of the 5 yuan system of this invention with dominant oxide ion conductivity (what is shown by y>=0.025, z<=0.15, and the above-mentioned ** formula is included) YSZ Since high oxide ion conductivity is shown, it is useful as a gas sensor, especially an oxygen sensor and low temperature or oxide ion conductivity is high, below 600 ** becomes a gas sensor usable enough.
[0053] Oxide ion conductor of the 5 yuan system of this invention with dominant oxide ion conductivity (what is shown by y>=0.025, z<=0.15, and the above-mentioned ** formula is included) It can be used also as a deoxygenation film for electrochemical oxygen pumping. If the potential difference is given to the both sides of the demarcation membrane which consists of an oxide ion conductor, oxide ion will move inside, current will flow and oxygen will come to flow from the field of one side in the one direction to the field of the opposite side. This is oxygen pumping. For example, if air is passed, since the air to which enrichment of the oxygen was carried out will be acquired from the field of the opposite side, it is used as a deoxygenation film.
[0054] Such deoxygenation films are for example, an aircraft for military affairs, a HEL, etc., and are used for making oxygen enrichment air from a surrounding subtle air. It is thought that there is an application possibility also as a substitute of a medical-application oxygen cylinder.
[0055] moreover, electronic-ion mixed conductivity (that is, the ion transference number 0.7 henceforth) 5/4 yuan system perovskite mold oxide ion conductor of shown this invention (z> 0.15) Since both sufficient oxide ion conductivity to function as electronic conduction nature required to function on oxygen as an ionization catalyst which carries out electronic grant, and

function as a charge collector as an oxide ion conductor for sending oxide ion into an electrolyte is shown It is suitable for the material of the air pole of SOFC mentioned above, and it is desirable to constitute a part of air pole [at least] from this material.

[0056] 5 yuan system material of this invention whose oxide ion conductivity which mentioned the electrolyte of SOFC above especially is the oxide ion conductor of a dominant narrow sense (** type -- y>=0.025 --) z<=0.15, the thing which is especially z<=0.10, and the thing shown by the above-mentioned ** formula are also included from, when it constitutes 5/4 yuan system material of this invention which shows electronic-ion mixed conductivity to the air pole (the thing of z> 0.15 and the case of y= 0 are included by ** formula) If it is used, materials with the electrolyte and air pole of SOFC of the same kind will be consisted of, and the engine performance of SOFC will improve.

[0057] If this point is explained in detail, at the conventional SOFC, the electrolyte and the air pole consist of materials of a different kind. [, for example, an electrolyte, is YSZ and an air pole is La(Sr) CoO3]. . In this case, if it sees microscopically on atomic level, the very thin volume phase to which the material of both layers was mixed with the interface of an electrolyte and an air pole will generate, and an output will decline for the voltage loss by that interfacial resistance. If an electrolyte and an air pole are constituted from a material of the same kind, generation of a volume phase will be controlled and interfacial resistance will become small.

[0058] Since in addition to the problem of interfacial resistance both coefficient of thermal expansion differs when an electrolyte and an air pole are materials of a different kind, the thermal stress added at the time of a temperature up and a temperature fall becomes large. This problem is also remarkably reduced by constituting an electrolyte and an air pole from a material of the same kind.

[0059] Above-mentioned interfacial resistance and thermal stress can be further controlled, if 1 or two or more interlayers with the middle presentation of these two materials are prepared between an electrolyte and an air pole and it is made for a presentation to change from an electrolyte to an air pole gradually.

[0060] Although a fuel electrode can be constituted from various materials used conventionally as mentioned above, especially the material of a desirable fuel electrode is (1). nickel and (2) General formula: Ce1-mCmO2 (the inside of a formula and C mean one sort of Sm, Gd, Y, and calcium, or two sorts or more, and are m=0.05-0.4) It consists of a compound shown. Both rate, (1) : (2) It is desirable that a volume ratio is within the limits of 95:5-20:80. M value more preferably It is 0.1-0.3, (1) : (2) Volume ratios are 90:10-40:60.

[0061] Especially the structure of SOFC may not be restricted, cylindrical or a plate mold may be used, and, in the case of a plate mold, any of a sintering mold (monolith type) are a stack mold and really sufficient. The layered product (one side touches an air pole layer and, as for an electrolyte layer, other sides touch a fuel electrode layer) of three layers which pinched the electrolyte layer with the air pole and the fuel electrode in any case becomes primitive cell structure. An electrolyte layer is gas impermeability, and each class of an air pole and a fuel electrode is porosity so that gas can be passed. In a cylindrical case, it divides into the cylindrical interior and the cylindrical exterior, fuel gas (an example, hydrogen) and air (or oxygen) are supplied separately, and many cylindrical cels are connected to it through the interconnector prepared in a part of the external surface. in the case of the plate mold, the passage which can supply fuel gas and air separately was prepared -- gas is supplied in general using the interconnector of a plate mold. This interconnector is accumulated by turns [the plate mold cel and by turns] which consist of the above-mentioned laminated structure of three layers, and it is multilayered.

[0062] One of the reactions which become rate-limiting by the electrode reaction of SOFC is ionization of the oxygen in the air pole shown by the degree type.

1/2O2+2e-->O2 - Since this reaction occurs by the interface of an air pole, an electrolyte, and air, reacting weight increases, so that the area of this interface is large. Therefore, it not being monotonous and, using the above-mentioned three-tiered structure object as a wave type for example, has so far been performed.

[0063] In the suitable mode of this invention, as shown in drawing 8 , irregularity is formed in both sides of an electrolyte layer, and the cellular structure which made the material of an air pole or a fuel electrode adhere to this surface irregularity section in the shape of a particle is used. In this case, although it is necessary to make the main part portion of an electrolyte layer into gas impermeability, the concavo-convex section formed on the surface of both sides may be porosity. the material as an electrolyte with the same material of this concavo-convex section (namely, oxide ion conductor in a narrow sense) ****** -- although -- it considers as the material in which electronic-ion mixed conductivity is shown preferably. for example, material in which the electronic-ion mixed conductivity which starts this invention in the concavo-convex section by the side of an air pole is shown (z> 0.15) from -- it can constitute. In that case, as for each particle made to adhere to this concavo-convex section, it is desirable that electron nature electric conduction like the conventional air pole material consists of dominant materials.

[0064] Such structure bakes an ion-electronic mixed conductor particle on the surface of an electrolyte layer first, next makes a detailed electronic conductor particle adhere by the surface further, and can be formed by baking. Or the same structure is realizable at a fixed rate also by making the mixture of an ion-electronic mixed conductor particle and an electronic conductor particle adhere to the surface of an electrolyte layer, and only baking it.

[0065] The material of the conventional air pole has dominant electron nature electric conduction, such as La(Sr) CoO3 and La(Sr) MnO3. (the ion transference number is low) Since it is an electronic conductor, even if it ionizes the oxygen in air to oxide ion, it cannot **, if it passes through the inside of an air pole material and oxide ion is sent into an electrolyte. Therefore, when using this air pole material, the surface irregularity section by the side of the air pole of drawing 8 is constituted from an electrolyte material, and an air pole material is made to adhere to this surface irregularity section in the shape of a particle. Ionization of the oxygen in that case is drawing 9 (a). It happens only in the single dimension-field which met the rim (circumference) of the interface of the three phase circuit of an electrolyte layer, an air pole particle, and air, i.e., the plane of composition of an electrolyte layer and an air pole particle, so that it may be shown. Consequently, polarization of an air pole becomes large and the fall of the output of SOFC takes place. Moreover, since the electrolyte layer needs to be in contact with air in order to incorporate oxide ion, an air pole cannot cover an electrolyte layer completely, but coating weight also has a limit. Therefore, the electrical installation to the external terminal depending on the electron nature electric conduction of an air pole also tends to become imperfect. Or although the structure of cross linkage which is rich in the opening of the electrical conducting material which covers a three-phase-circuit interface to **, and connects air pole particles is needed in order to obtain sufficient electrical installation, the opening structure is resisting to passage of gas in that case.

[0066] On the other hand, since the material of the air pole of this invention shows ion-electronic mixed conductivity, this material itself can ionize the oxygen in air to oxide ion. Therefore, as mentioned above, the surface irregularity section by the side of the air pole of drawing 8 can be constituted from an air pole material of this mixed conductivity, and each particle made to adhere to this concavo-convex section can consist of air pole materials of the conventional electronic conductor. Since ionization efficiency increases by leaps and bounds since it happens in a 2-dimensional field called the surface irregularity section of a mixed conductivity material and the whole interface of two phases of air, i.e., the outside surface of this material, and ionization of the oxygen in that case can prevent polarization of an air pole

as shown in drawing 9 (b), its output of SOFC improves. The oxide ion generated by ionization is transmitted in an air pole material with the oxide ion conductivity of this mixed conductivity air pole material, and flows to an electrolyte. Moreover, in order to help it, the particle of an electronic conductor is made to adhere to the surface of the concavo-convex section by the side of an air pole, although electron nature electric conduction is also possible for the mixed conductivity air pole material which forms this surface irregularity section and the electrical and electric equipment can be passed for an external terminal.

[0067] a fuel electrode -- above -- nickel and the Seria system material (Ce1-mCmO2) from -- constituting is desirable. Also in this case, the Seria system material which is an oxide ion mixed conductor constitutes the surface irregularity section by the side of a fuel electrode, and each particle of that surface consists of nickel which is an electronic conductor. Like the case of the air pole mentioned above by this configuration, carrier delivery of the oxide ion of H2 is performed in a two-dimensional field, and it is H2O too. The effectiveness of a generation reaction improves remarkably.

[0068] Oxide ion conductor of this invention in which electronic-ion mixed conductivity is shown (z> 0.15) It can use also as a gas separation membrane using a gas concentration difference. It is not necessary to give the potential difference from the exterior to membranous both sides, and, in the case of a gas separation membrane, the oxygen density difference in the gas of the both sides of a demarcation membrane serves as driving force of separation. In order for oxide ion to flow to the method low concentration side of a high concentration side and to compensate this flow electrically according to this oxygen density difference, an electron flows to hard flow. therefore -- there are not oxide ion conductivity and a certain amount of [together] electron nature electric conduction, either (namely, -- it is not an electronic-ion mixed conductor) It stops functioning, in order that an electron may not flow.

[0069] This gas separation membrane is not only oxygen but water, and NOX. It can be used also for decomposition. If it decomposes into oxide ion and hydrogen on the surface of a demarcation membrane in the case of water, since a difference is made to oxide ion concentration on membranous both sides, this will serve as driving force, the flow of oxide ion will be made and hydrogen will remain, without flowing, hydrogen can be manufactured from water. NOX A case is also decomposed and it is NOX. It is defanged and separates into nitrogen and oxygen.

[0070] In addition, the oxide ion conductor of this invention is available on an electrochemical reactor, an oxygen isotope separation film, etc.

[0071]

[Example] La 2O3, SrCO3, Ga 2O3, and MgO, (Example 1) And each powder of CoO, Fe 2O3, nickel 2O3, CuO, and the transition-metals oxide chosen from MnO2 La0.8 Sr0.2 Ga0.8 Mg 0.1M0.1O3 (M is transition metals) After blending at a rate to produce and often mixing, preliminary baking was carried out at 1000 degrees C for 6 hours. This mixture that carried out preliminary baking is ground, and they are thickness 0.5 mm and diameter 15 mm by the hydrostatic-pressure press. It presses in the shape of a disk, and the Plastic solid was calcinated for 6 hours and made to sinter at 1500 degrees C. When the X diffraction investigated the crystal structure of the obtained sintered compact, all had the perovskite mold crystal structure.

[0072] After applying the platinum paste used as an electrode to the rectangular parallelepiped sample cut from the sintered compact of a disk form, the electrical conductivity of the obtained sintered compact connected the platinum wire, could be burned for 10 - 60 minutes at 950-1200 degrees C, and was searched for by measuring resistance within the equipment which can be adjusted to the oxygen tension and temperature of arbitration by the direct-current four probe method or the alternating current one terminal pair network method. Adjustment of oxygen tension is O2-N2, CO-CO2, and H2-H2O. It carried out using mixed gas.

[0073] A measurement result is shown in drawing 2 and drawing 10. Oxygen tension of drawing 2 is fixed. (10-5 atm) Electrical conductivity at the time of changing temperature (Arrhenius plot of conductivity) It is shown. Temperature of drawing 10 is fixed. (950 **) Electrical conductivity at the time of changing oxygen tension (oxygen tension dependency of conductivity) It is shown. Although drawing 2 was already explained, by replacing some Mg with transition metals as transition metals are Co, Fe, nickel, or Cu shows that conductivity improves greatly in a low temperature side at least.
[0074] Although conductivity is changed by oxygen tension as transition metals are nickel, Cu, or Mn, drawing 10 shows holding high, almost fixed conductivity, even if it changes oxygen tension as transition metals are Co or Fe.
[0075] About the compound whose transition metals are Co, the result of having measured the ion transference number is shown in drawing 5 together with conductivity. It searched for the theoretical electromotive force of these conditions from the Nernst equation, and searched for it as a ratio to the theoretical electromotive force of the measured value of electromotive force while this ion transference number made the oxygen tension of the ambient atmosphere of the both ends of a sample a mutually different known value, produced the oxygen concentration cell and measured the electromotive force of this cell by partition. Even if transition metals were except Co, when the almost same orientation as drawing 5 was accepted and the rate of transition metals to Mg increased, electrical conductivity increased and the ion transference number fell. However, since increase of electrical conductivity is pair numerical increase, it is much larger than decline in the ion transference number. Therefore, even if the ion transference number falls, the absolute value of oxide ion conductivity is increasing.
[0076] (Example 2) The oxide ion conductor which consists of a sintered compact of La0.8 Sr0.2 Ga0.8 Mg0.115 Co 0.085O3 was produced like the example 1, temperature was changed by oxygen tension 10-5 atm, and electrical conductivity was measured. Measurement result (Arrhenius plot of conductivity) It is shown in drawing 11.
[0077] (Example 3) The oxide ion conductor which consists of a sintered compact of La1-x Srx Ga0.8 Mg0.115 Co 0.085O3 (xin formula =0. 05, 0.1, 0. 15, 0.2, 0.25 or 0.3) was produced like the example 1, temperature or oxygen tension was changed, and electrical conductivity was measured. 950 The relation of the value of x and electrical conductivity in ** is shown in drawing 3 . Arrhenius plot of conductivity (oxygen tension 10-5 atm) Oxygen tension dependency (temperature 950 **) It is drawing 12 (a), respectively. And it is shown in (b). That an action changes with x values attracts attention to an oxygen tension dependency.
[0078] (Example 4) The oxide ion conductor which consists of a sintered compact of La0.8 Sr0.2 Ga (1-y-z) Mgy Coz O3 (inside of a formula, y+z=0. 05, 0.1, 0. 15, 0.2, 0.3 [0.25 or 0.3], y:z= 11.5:8.5) was produced like the example 1, temperature was changed, and electrical conductivity and the ion transference number were measured. ** (y+z) Arrhenius plot of the conductivity in a value (oxygen tension 10-5atm) Drawing 4 (c) It is shown. 950 it can set to ** (y+z) the relation between a value and electrical conductivity -- drawing 4 (a) -- moreover, relation with the ion transference number -- drawing 4 (b) It is shown.
[0079] (Example 5) It is Ln0.9 A0.1 Ga0.8 B10.1 Co 0.1O3 like an example 1. By the presentation, the oxide ion conductor which consists of a sintered compact which changed each metal atom of Ln, A, and B1 was produced, and the electrical conductivity was measured. Electrical conductivity in oxygen tension 10-5 atm and 950 ** (sigma/Scm -1) It was as follows.
[0080] ** Ln0.9 Sr0.1 Ga0.8 Mg0.1 Co0.1 O3
Ln=La:0.53=Pr:0.49=Nd:0.36=Ce:0.08=Sm:0.05**La0.9 A0.1 Ga0.8 Mg0.1 Co0.1 O3
A=Sr:0.53=calcium:0.24=Ba:0.22**La0.9 It is made to be the same as that of the Sr0.1 Ga0.8 B10.1 Co0.1 O3B1=aluminum:0.12=Mg:0.53=In:0.23 (example 6) example 1. The oxide ion conductor which consists of a sintered compact of La0.8Sr0.2Ga0.8Mg0.2-zFez O3 (z=0-0.2)

was produced. When the X diffraction investigated the crystal structure of the obtained sintered compact, all had the perovskite mold crystal structure.

[0081] The measurement result of the electrical conductivity in temperature 950 ** of this oxide ion conductor and oxygen tension 10-5 atm is as having been shown in drawing 6 . This drawing shows that electrical conductivity high in within the limits of z=0.01-0.15 is acquired as mentioned above. Moreover, it sets to the above-mentioned presentation and the temperature change and oxygen tension dependency of electrical conductivity of z= 0.03 are drawing 7 (a), respectively. And (b) It is as having been shown. [of a case] It turns out that this oxide ion conductor shows electrical conductivity high in a large temperature requirement and the range of oxygen tension, and the ion transference number.

[0082]

[Effect of the Invention] According to this invention, even if compared with the 4 yuan system multiple oxide which doped only non-transition metals, of course to A site where oxide ion conductivity is higher than it, and B site, that oxide ion conductivity is higher than the stabilized zirconia which is the conventional typical oxide ion conductor has still higher oxide ion conductivity, and it can realize the oxide ion conductor which can control easily and freely the rate of oxide ion conductivity and electronic conduction nature, i.e., the ion transference number. Therefore, electrical conductivity is high and the ion transference number is 0.9. Not only a material useful as the above and a high oxide ion conductor in a narrow sense but a material useful as an electronic-ion mixed conductor is obtained.

[0083] Since the oxide ion conductor of this invention with the high ion transference number shows high oxide ion conductivity by all the oxygen-content drafts from an oxygen ambient atmosphere to [can use it also at low temperature from stabilized zirconia, and] a hydrogen ambient atmosphere, it is useful as gas sensors, such as an electrolyte of a solid acid ghost mold fuel cell, and an oxygen sensor, and a deoxygenation film for electrochemistry type oxygen pumping, and may be able to realize the product of high performance conventionally. Especially the oxide ion conductor shown by the above-mentioned ** formula is very advantageous at the point of holding high oxide ion conductivity by the very large oxygen tension which attains to a substantial hydrogen ambient atmosphere from a large temperature requirement and a pure oxygen ambient atmosphere.

[0084] Moreover, the oxide ion conductor of this invention in which electronic-ion mixed conductivity is shown can be used as the air pole of a solid acid ghost mold fuel cell, and a gas separation membrane using a gas concentration difference. If the oxide ion conductor of this invention in which this electronic-ion mixed conductivity is shown especially is made into an air pole and SOFC is built by using the oxide ion conductor of the narrow sense concerning this invention with the above-mentioned high ion transference number as an electrolyte, since interfacial resistance will decrease, the high increase in power of SOFC can be attained.

[Translation done.]